Transformation of monuron photosensitized by soil extracted humic substances: energy or hydrogen transfer mechanism?

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Abstract

The humic and fulvic acids extracted from a Ranker type soil sensitize the transformation of monuron. When monuron is irradiated at 365 nm in the presence of the fulvic acid, its degradation is faster in deoxygenated medium than in air-saturated solution. Chloride ions are released, and the *para*-hydroxylated derivative is formed as upon direct photolysis. It is deduced that the consumption of monuron observed in the absence of oxygen is due to an energy transfer from reactive triplet states of the fulvic acid to monuron. Energy transfer reactions also take place when hydroquinone or acetophenone are used as sensitizers, showing that the energy level of the triplet state of monuron is lower than 311 kJ mol^{-1}. The rate of monuron disappearance in the presence of the humic acid is lower in deoxygenated than in aerated medium. This oxygen effect indicates that there is no energy transfer. A hydrogen atom transfer from monuron to triplet states of the humic acid probably takes place.   © 1997 Elsevier Science S.A.

Keywords: Fulvic acid: Humic acid: Monuron; Fenuron; 4-Chloroacetanilide; Phototransformation

1. Introduction

Humic substances are natural organic materials which are now recognized to play an important role in the photochemical processes occurring in surface waters [1]. They photoinduce the transformation of a great variety of organic compounds, however, the mechanisms of the reactions often remain unclear. It is now established that singlet oxygen and hydroperoxyl radical/superoxide anion are produced upon irradiation of humic substances [2–11]. These species are responsible for the transformation of various but specific substrates. Recently, the humic substances-mediated transformation of phenolic derivatives was studied in detail [12–15]. It was demonstrated that the degradation of phenols is mainly due to a direct reaction with oxidant triplet states of humic substances through electron or hydrogen atom transfer [13,14]. Reactive triplet states of humic substances should also be able to sensitize the degradation of organic compounds through electronic energy transfer. However, to our knowledge, only the photoisomerizations of 1,3-pentadiene [2,5] and cinnamic esters [16] were shown to be sensitized by humic substances.

The phototransformation of the herbicide fenuron (1,1-dimethyl-3-phenyl-urea) was reported to be photoinduced by humic substances [17]. This reaction has the following characteristics. First, the photoproducts are the *para*-hydroxylated derivative and biphenyls; they are therefore different to those obtained by direct photolysis (4 and 2-amino-*N*,*N*-dimethyl-benzamide). Second, the effect of oxygen on the reaction is the same as that observed in the case of phenol derivatives: the transformation of fenuron is much faster in air-saturated solution than in deoxygenated medium and smaller in oxygen-saturated medium than in air-saturated solution. Since fenuron does not react with singlet oxygen, a mechanism similar to that proposed in the case of phenol derivatives [14] was suggested (Scheme 1). This explains the important role played by oxygen in the reaction.

To gain a better insight into the parameters governing the hydrogen abstraction by triplet states of humic substances, we investigated the photoinduced transformation of monuron, the *para*-chloro-substituted derivative of fenuron. The first results showed that the mechanism of the reaction was different to that observed in the case of fenuron and suggested that an energy transfer rather than a hydrogen atom transfer occurred. A detailed study was therefore carried out in order to establish whether an energy transfer mechanism was operating with monuron. In this way, we studied the photosensi-

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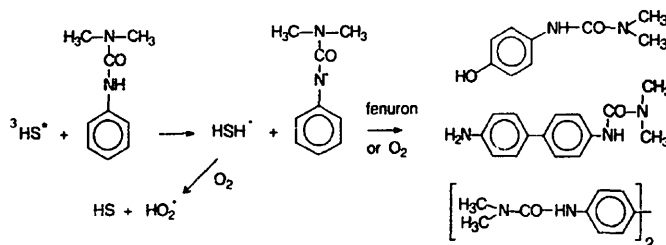
Scheme 1.

tized transformation using both humic substances and model sensitizers such as hydroquinone and acetophenone to obtain information on the energy level and on the reactivity of the triplet state of monuron. The humic and fulvic acids used in this study were extracted from the organic-rich horizon of a Ranker type soil, as explained in a former paper [18]. Some experiments were also undertaken with 4-chloroacetanilide, the chemical structure of which is close to that of monuron.

monuron (M)   4-chloroacetanilide (4-ClA)
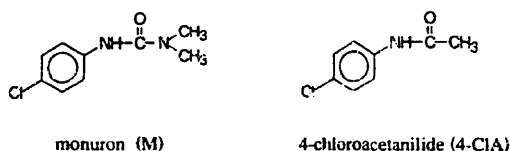
2. Experimental part

Fenuron (F), monuron (M), 4-chloroacetanilide (4-ClA), hydroquinone (QH₂), acetophenone (AP) and 4-hydroxyacetanilide were of the highest grade available and used without further purification. Water was purified with a Milli-Q device (Millipore). Humic acid (HA) and fulvic acid (FA) were extracted by a standard procedure [19] from the surface (A1) horizons of a mountain acid soil Ranker.

The solutions containing the humic substances and the substrates were buffered at pH 6.5 with phosphates, filtered through 0.45 μm Millipore filters prior to irradiation and irradiated at 365 nm in a water-cooled reactor using three 'black-light' lamps (HPW 125 W Philips) and a cylindrical reactor. Substrates were irradiated in the absence of sensitizers using a device equipped with three fluorescent tubes (Duke sun lamp FL20E) emitting within the range 280–350

nm with a maximum located at 310 nm. Solutions containing substrates and hydroquinone or acetophenone were irradiated in the same device but in a glass reactor to cut off the wavelengths shorter than 300 nm and prevent M and 4-ClA from light absorption. Deoxygenation of solutions was performed either by three cycles of freezing-pumping-thaw on a vacuum line or by nitrogen bubbling.

Solutions were analysed by high performance liquid chromatography (HPLC) on a Waters chromatograph equipped with a photodiode array detector (model 990) and a C18 Lichrosphere column (5 μm, 125 mm × 4 mm) supplied by Merck. Chloride ions were titrated with an Orion chloride specific electrode. To increase the precision of measurements, solutions were concentrated by evaporation.

3. Results

3.1. Direct photolyses of M and 4-ClA

The direct photolysis of M was previously studied by several authors [20–24]. The quantum yield of loss of M was found to be 0.1. Many photoproducts were identified, especially at high monuron concentration and high conversion extent (> 30%), but ring hydroxylation and dimerization were the main processes [21,22]. In the presence of surfactants or alcohols, the reduction product fenuron was mainly formed [23,24].

To complement these studies, we irradiated M (2 × 10⁻⁴ M) with sun lamps in a pyrex reactor and in the absence of oxygen. Under these conditions, we observed the formation of chloride ions (chemical yield 60%) and found the para-hydroxylated derivative as the major photoproduct (chemical
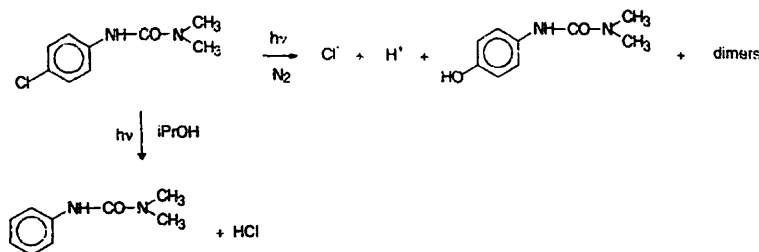
Scheme 2.

Table 1
Transformation of the substrates (2×10^{-4} M) sensitized by hydroquinone (10^{-3} M) or acetophenone (4×10^{-5} M); excitation at $\lambda > 300$ nm

Substrate	Sensitizer	Irradiation time	Substrate consumed (M)	Sensitizer consumed (M)
M, deoxygenated medium	QH_2	10 min	1.2×10^{-4}	0.35×10^{-3}
M, oxygen-saturated solution	QH_2	10 min	$<0.1 \times 10^{-4}$	0.10×10^{-3}
4-ClA, deoxygenated medium	QH_2	5 min	0.7×10^{-4}	0.10×10^{-3}
F, deoxygenated medium	QH_2	5 min	$<0.1 \times 10^{-4}$	not measured
M, deoxygenated medium	AP	2 h	0.2×10^{-4}	0.05×10^{-4}
M, oxygen-saturated solution	AP	2 h	$<0.1 \times 10^{-5}$	0.09×10^{-4}
4-ClA, deoxygenated medium	AP	2 h	0.8×10^{-4}	0.04×10^{-4}
4-ClA, oxygen-saturated solution	AP	2 h	$<0.1 \times 10^{-5}$	0.02×10^{-4}
F, deoxygenated medium	AP	2 h	0.19×10^{-4}	0.18×10^{-4}
F, oxygen-saturated solution	AP	2 h	0.08×10^{-4}	0.18×10^{-4}
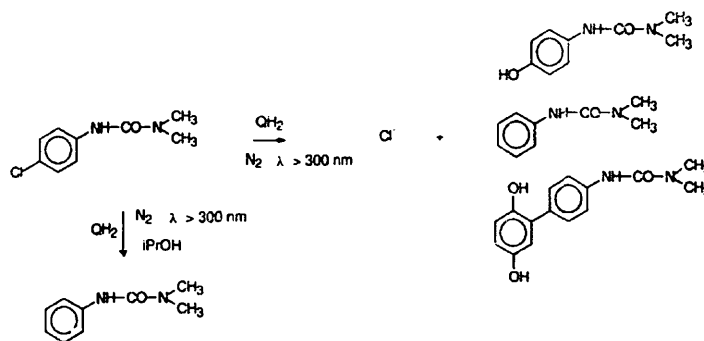
Scheme 3.

yield 30%) (Scheme 2). In accordance with the release of HCl, the pH of the solutions decreased during irradiation. When 2-propanol was added to the reaction mixtures, fenuron was the main photoproduct. The reaction is described in Scheme 2.

Two photoproducts were formed when 4-ClA was irradiated within the wavelength range 280–300 nm. One was the hydroxy derivative (4-hydroxyacetanilide). Its formation was inhibited by 2-propanol (1%). The other photoproduct was extracted in ether and analysed by GCMS. It showed $m/z = 169$ and 171 with fragments at 154, 156 and 126, 128. The formation of this compound was affected neither by oxygen nor by 2-propanol. It can be assigned to 2'-amino-5'-chloroacetophenone which is expected to result from a photo-fries rearrangement.
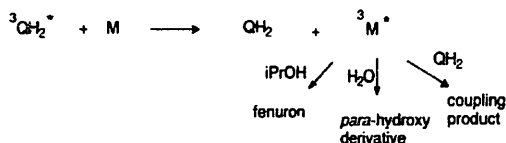
3.2. Transformations sensitized by hydroquinone and acetophenone

Hydroquinone (QH_2) has the properties of a good sensitizer ($\phi_T = 0.39$, $\tau_T = 1.3$ μs [25] and $E_T = 311$ kJ mol^{-1} [26]) and was shown to sensitize the transformation of several halogenophenols [27]. Deoxygenated solutions containing QH_2 (10^{-3} M) and M (2×10^{-4} M) were irradiated at $\lambda > 300$ nm in order to excite selectively QH_2. After 10 min irradiation, 60% of monuron was transformed and QH_2 was recovered at 90% (Table 1). It can be concluded that QH_2

sensitizes the transformation of M because, when M is irradiated alone under the same conditions, no reaction is observed. The photoproducts resulting from the QH_2-sensitized reaction were analysed. Along with the para-hydroxylated derivative, formed in very small amounts, fenuron and a third photoproduct were observed (Scheme 3). This latter product was separated by semi-preparative HPLC and analysed by NMR and GCMS. From the data following, it was assigned to the coupling product. ^{1}H NMR δ (CD$_3$OD): 3.22 (s, 6H), 6.78 (dd, 1H, $J = 8.5$ Hz and $J = 2.9$ Hz), 6.89 (d, 1H, $J = 2.9$ Hz), 6.91 (d, 1H, $J = 8.5$ Hz), 7.57 (d, 2H, $J = 8.7$ Hz), 7.65 (d, 2H, $J = 8.7$ Hz). MS m/z: 272. The formation of this product explains the loss of QH_2. The rate of Cl$^-$ formation was found to be equal to the rate of monuron consumption.

Mixtures QH_2–monuron were also irradiated in the presence of 2-propanol (1%). Under these conditions, the photoproducts changed: fenuron became the main photoproduct, the formations of the coupling product and of the 4-hydroxyderivative being drastically inhibited (Scheme 3). Upon irradiation of QH_2–monuron mixtures in oxygen-saturated solutions, monuron was not transformed, in accordance with the quenching of triplet hydroquinone by oxygen.

All these results indicate that an energy transfer process occurs, yielding the triplet excited state of monuron. The pattern of the reaction is the same as that observed in direct photolysis. Since QH_2 is more concentrated than monuron, a

$$^3QH_2{}^* + M \longrightarrow QH_2 + {}^3M{}^*$$

iPrOH / H₂O ↓ \ QH₂

fenuron   para-hydroxy   coupling
           derivative   product

Scheme 4.

coupling product between dechlorinated M and QH_2 is formed in place of dimers of M (Scheme 4).

QH_2 sensitized the transformation of 4-ClA (Table 1). The photoproducts formed were 4-hydroxyacetanilide, acetanilide and a compound assigned to a coupling product. It can be concluded that here again there is energy transfer from triplet hydroquinone to ground state 4-ClA. The photoproduct resulting from the photo-fries rearrangement (2'-amino-5'-chloroacetophenone) and observed in direct photolysis was not produced by sensitization. It is therefore probably formed from the singlet excited state.

No consumption of fenuron (F) occurred upon irradiation of deoxygenated mixtures containing QH_2 (10^{-3} M) and F (2×10^{-4} M) (see Table 1). So, there was no energy transfer in this case or the triplet state of F was unreactive.

In the absence of oxygen, AP sensitized the transformation of M, 4-ClA and F (see Table 1). The consumption of AP was very small compared with that of M and 4-ClA, in accordance with an energy transfer. By contrast, the consumption of AP equalled that of F, indicating that a hydrogen atom transfer occurs leading to the oxidation of fenuron and to the reduction of acetophenone. It was previously shown that the same photoproducts are formed when fenuron is irradiated in the presence of acetophenone or humic substances [17].

3.3. Transformations photosensitized by humic substances

No consumption of M was observed when it was irradiated alone at 365 nm with black light lamps. By contrast, M was degraded when it was irradiated in the presence of FA or HA (Fig. 1, Table 2). Results in Table 2 are expressed in rates and not in quantum yields because quantum yields cannot be measured accurately in our experimental device. Since the irradiations were performed in the same device with the same lamps, the quantitative data can be compared. With HA, the consumption of M was about three times as fast in air-saturated solutions as in deoxygenated medium and twice as slow in oxygenated medium as in air-saturated solution. By contrast, with FA, the rate of M disappearance increased as the concentration of oxygen decreased, the rate of transformation in the absence of oxygen being about twice that observed in air-saturated solution. Whatever the oxygen concentration, the rates of monuron transformation were at least three times higher with FA than with HA although the absorbance at 365 nm of FA is smaller than that of HA (0.17 instead 1.0 for 100 mg l^{-1}).

Upon irradiation of deoxygenated solutions containing monuron and FA, chloride ions were released, and the rate of Cl^- formation was equal to the rate of monuron consumption. 4-hydroxyderivative which was previously characterized [17] was the only organic compound detected. It represented only 10% in moles of the converted monuron. It can be assumed that the main part of organic photoproducts are chemically linked to FA and therefore not detectable using our analytical conditions. When 2-propanol was added to the reaction mixture, the rate of M transformation decreased significantly (see Table 1) and a change in the photoproducts occurred: fenuron was formed instead of 4-hydroxyderivative. In irradiated samples containing 2-propanol (1%), the 4-hydroxyderivative is not produced and the chemical yield of fenuron reached 50%, indicating that the formation of fenuron is competitive with both the hydroxylation process and the addition on FA.

When deoxygenated mixtures of HA–monuron were irradiated, 4-hydroxyderivative was detected as previously.
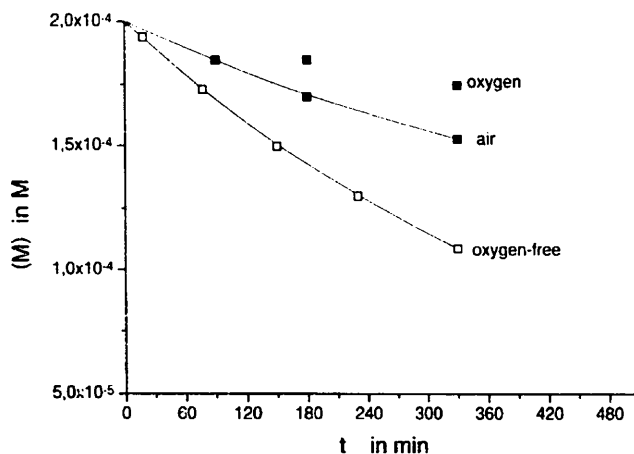

Fig. 1. Concentration of M as a function of the irradiation time in mixtures of FA (100 mg l^{-1}) and M (2×10^{-4} M), pH 6.5: □ deoxygenated solution; ■ air-saturated solution; – ■ – oxygen-saturated solution.

Table 2

Rates of F (2×10^{-4} M), M (2×10^{-4} M) and 4-ClA (2×10^{-4} M) consumption in the presence of FA (absorbance at 365 nm equal to 0.17 with 100 mg l^{-1} FA and to 1.0 with 100 mg l^{-1} HA). $\lambda_{exc} = 365$ nm

	Conditions	Rate (M s^{-1})
Fenuron	HA 100 mg l^{-1} deoxygenated	1.3×10^{-9}
	HA 100 mg l^{-1} air-saturated	9.0×10^{-9}
	HA 100 mg l^{-1} oxygen-saturated	3.1×10^{-9}
	FA 50 mg l^{-1} deoxygenated	1.7×10^{-8}
	FA 50 mg l^{-1} air-saturated	1.0×10^{-8}
	FA 50 mg l^{-1} oxygen-saturated	3.8×10^{-9}
Monuron	HA 100 mg l^{-1} deoxygenated	0.3×10^{-9}
	HA 100 mg l^{-1} air-saturated	1.0×10^{-9}
	HA 100 mg l^{-1} oxygen-saturated	0.6×10^{-9}
	FA 100 mg l^{-1} deoxygenated	5.8×10^{-9}
	FA 100 mg l^{-1} air-saturated	2.7×10^{-9}
	FA 100 mg l^{-1} oxygen-saturated	1.4×10^{-9}
	FA 50 mg l^{-1} deoxygenated	2.8×10^{-9}
	FA 50 mg l^{-1} air-saturated	1.5×10^{-9}
	FA 50 mg l^{-1} oxygen-saturated	0.6×10^{-9}
	FA 100 mg l^{-1} deoxygenated, iPrOH (0.01%)	1.5×10^{-9}
	FA 100 mg l^{-1} deoxygenated, iPrOH (0.1%)	0.7×10^{-9}
	FA 100 mg l^{-1} deoxygenated, iPrOH (1%)	0.2×10^{-9}
4-Chloroacetanilide	FA 50 mg l^{-1} deoxygenated	2×10^{-10}
	FA 50 mg l^{-1} air-saturated	2.5×10^{-10}
	HA 100 mg l^{-1} air-saturated	1×10^{-10}

However, the presence of 2-propanol did not cause a change in photoproducts was observed in FA–monuron mixtures.

4-ClA disappeared very slowly upon irradiation in the presence of FA or HA. The rates of transformation were found to be 10 to 40 smaller than that of F and M.

For comparison, F was also irradiated in the presence of FA and HA. Results are given in Table 2 and Fig. 2. With FA or HA, the initial rates of F consumption were about five times as high in air-saturated solutions as in deoxygenated medium. These results resemble those obtained with HA–monuron mixtures. In the presence of HA, F disappeared up to nine times faster than M.

4. Discussion

We show that the humic and fulvic acids used in this study sensitize the transformation of monuron. Analysis of all the data prompts us to deduce that two different types of reaction take place: an energy transfer process in the system FA–monuron and a hydrogen atom transfer in the system HA–monuron.

First, oxygen affects differently the two reactions. The FA-sensitized transformation of monuron is faster in deoxygenated medium than in air-saturated solution, whereas the HA-sensitized transformation of monuron is faster in the
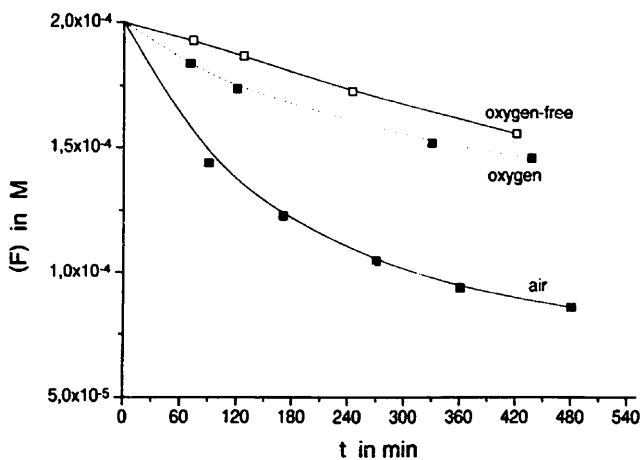

Fig. 2. Concentration of F as a function of the irradiation time in mixtures of FA (50 mg l^{-1}) and F (2×10^{-4} M), pH 6.5: □ deoxygenated solution; ■ air-saturated solution; – ▨ oxygen-saturated solution.

presence than in the absence of oxygen. This latter oxygen effect was previously reported in the sensitized transformations of fenuron [17] and of phenolic compounds in the presence of various humic substances [13,14]. It was observed that without oxygen almost no reaction takes place and that the rates of transformation are lower in oxygen-saturated than in air-saturated solutions. By analogy to results obtained with model carbonyl sensitizers, it was suggested that reactive excited triplet states of humic substances abstract an electron or a hydrogen atom from the phenolic substrates [14]. The hydrogen atom is then transferred onto oxygen which is reduced into hydroperoxyl radical or superoxide anion; oxygen is thus needed for the chromophores to be regenerated. At high concentration oxygen quenches efficiently the triplets and inhibits the consumption of substrates.

Clearly, the FA-sensitized transformation of monuron cannot only be explained by a hydrogen atom transfer reaction. Since oxygen inhibits the transformation of M, it can be suggested that an energy transfer process is likely to occur.

Second, the analogies in the photoproducts obtained in direct photolysis and upon irradiation of mixtures hydroquinone–monuron and fulvic acid–monuron in deoxygenated aqueous solutions are in accordance with this assumption. The photochemical behaviour of monuron through direct or hydroquinone-sensitized excitation can be described as follows. The nature of the organic photoproducts depends on the reactants present in solution, but, in every case HCl is released. The para-hydroxylated derivative and dimers are formed when monuron is irradiated alone. In the presence of hydroquinone, a coupling product between hydroquinone and dehalogenated monuron is produced instead of dimers. Finally, the reductive product fenuron is formed in the presence of 2-propanol instead of the above mentioned products. All these results show that the photoreactivity of monuron resembles that of 4-chlorophenol [28]. It can therefore be suggested that after loss of HCl a carbene-like intermediate is produced, this species tending to add on aromatic ring or to abstract a hydrogen atom from H-donor molecules. When monuron is irradiated in the presence of the fulvic acid, a chloride ion is released for each molecule of monuron converted and the main organic photoproduct detected (para-hydroxylated derivative) is formed in small amounts. Here again, the addition of 2-propanol leads to the formation of fenuron with a good chemical yield. All these results are similar to those obtained in direct photolysis or in sensitized reactions. The very poor yield in organic photoproducts may be explained by the addition of the carbene-like intermediate on the fulvic acid with formation of adducts not separated by HPLC.

By contrast, when mixtures containing HA, monuron and 2-propanol are irradiated, fenuron is not produced. This result confirms that the mechanisms of reaction in HA–monuron and FA–monuron mixtures are different.

Humic substances photoinduce very inefficiently the degradation of 4-chloroacetanilide. This means that both hydrogen atom and energy transfers are very difficult reactions.

The presence of a chlorine atom in para position with respect to the nitrogen contributes to reinforce the N–H, bond making abstraction of the hydrogen atom difficult. The abstraction of the hydrogen atom of monuron is difficult too. The rate of monuron consumption in the presence of HA is five to nine times smaller than that of fenuron. The same tendency is observed in aerated or oxygenated mixtures containing monuron and FA. In deoxygenated medium containing FA, the rate of monuron disappearance is higher than that of fenuron. It is clear that in this latter case, a hydrogen atom transfer mechanism cannot be invoked.

Taking into account that samples are irradiated at 365 nm and that singlet states are first produced, the energy of the humic substances triplet states produced must be much lower than 325 kJ mol^{-1}. It was previously shown that in humic substances half of the triplets have an energy higher than 250 kJ mol^{-1} [5]. It seems reasonable to consider that compounds with energy triplet states around or lower than 300 kJ mol^{-1} could react by energy transfer. Both hydroquinone and acetophenone sensitize by energy transfer the transformations of monuron and 4-ClA. The energy level of the triplet states of 4-ClA and monuron are thus lower than 311 kJ mol^{-1}. It is only with the system FA–monuron that an energy transfer occurs. This might reflect that the energy level of the triplet state of 4-ClA is higher than that of monuron. The reasons why fulvic acid sensitizes the transformation of monuron, whereas humic acid does not, are not clear. It may be due to energetic differences in triplet states of the humic substances.

5. Conclusion

The transformation of monuron is sensitized by the humic and fulvic acids extracted from a Ranker type soil. When monuron is irradiated in the presence of humic acid at 365 nm, its rate of consumption is higher in air-saturated medium than in deoxygenated solution as was previously observed with fenuron. It is concluded that in this case a hydrogen atom transfer between oxidant excited states of humic acid and monuron occurs. By contrast, with the fulvic acid, the consumption of monuron is faster in deoxygenated medium than in aerated solution. Moreover, the photoproducts are the same as those obtained either in direct photolysis or in the hydroquinone-sensitized transformation. It is therefore suggested that the fulvic acid sensitizes the degradation of monuron by an energy transfer process.

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